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Synthesis of phenothiazine-functionalized porphyrins with high fluorescent quantum yields

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ABSTRACT

Two porphyrins with oligo-phenothiazine arms have been synthesized by a combination of Heck and Adler reaction, and their photophysical properties have been investigated by absorption and steady-state fluorescence spectroscopy. It is found that the excitation energy transfer occurs from the phenothiazine units to the porphyrin core, and that the porphyrins can emit intense red light with high fluorescent quantum yields.

There has been continuous interest in the synthesis of porphyrins because of their wide potential applications in catalysis, medicine, photochemical energy conversion, switches, and molecular electronics.[1] It is well known that the peripheral substituents on the porphyrin core not only can modulate the physical properties, but also can impart the desired chemical characteristics to the macrocycle. Recently, a series of linear π-conjugated oligomers, such as oligofluorenes, oligo-*p*-phenylenevinylenes, oligothiophenes, and oligocarbazoles, have been introduced into the porphyrin core to build star-shaped porphyrins,[2] which are good candidates for photoinduced energy transfer systems and fluorescence emitting materials.[3,2a,f] On the other hand, phenothiazine is a recognized pharmaceutical compound bearing electron-rich sulfur and nitrogen heteroatoms, and the phenothiazine ring is nonplanar with a butterfly conformation in the ground state, which can impede the molecular aggregation and the formation of intermolecular excimer. Thus, phenothiazine maybe a potential p-type (hole transport) semiconductor in organic devices, presenting unique electronic and optical properties.[4] Therefore, if oligophenothiazine is introduced into the porphyrin, its excitation energy may transfer to the porphyrin ring, showing interesting photophysical properties. To the best of our knowledge, there is no report on the synthesis of the phenothiazine-functionalized porphyrin. In this Letter, we designed and prepared two new porphyrins using phenothiazine or diphenothiazine units as the arms in the *meso*-positions. It is found that the excitation energy transfer occurs from the phenothiazine arms to the porphyrin core, and both compounds can emit intense red light in solution as well as in the film with the fluorescent quantum yields of 0.35–0.40, which are higher than most porphyrins reported.[2a,h,3b]

The synthetic routes for the phenothiazine-functionalized porphyrins are shown in Scheme 1. Firstly, we synthesized the aldehyde precursors, compounds **4** and **5** via Heck reaction from compounds **1** and **3**, respectively. The Heck coupling reaction between compound **1** and *p*-iodobenzaldehyde was carried out at 110 °C for 15 h in DMF using $Pd(OAc)_2$ and tetrabutylammonium bromide as the catalysts, affording compound **4** in a yield of 85%. Compound **5** could be gained in a yield of 70% under similar Heck coupling condition. In addition, compounds **1**–**3** were synthesized according to the methods reported previously.[5d] The porphyrins **OPTZP1** and **OPTZP2** with phenothiazine arms were synthesized via Alder reaction in the mixed solvents of propionic acid, acetic acid, and nitrobenzene[6] because we found that only traces of **OPTZP1** and **OPTZP2** were obtained when the reaction was taken place in propionic acid alone or in xylene using *p*-nitrobenzoic acid as the catalyst.[7,2h] Finally, the porphyrins **OPTZP1** and **OPTZP2** in the yields of 18% and 15%, respectively, were gained in the mixed solvents at 135 °C for 2 h, and they had good solubility in common solvents, such as tetrahydrofuran, toluene, and dichloromethane. All the intermediates and the final products were purified by column chromatography. The molecular structures were characterized with FT-IR, ^{1}H NMR, elemental analysis, and MALDI/TOF mass spectroscopy.[8] The porphyrins and the corresponding aldehyde precursors exhibited an IR absorption band around 960 cm^{-1} arising from the wagging vibration of the *trans*-double bond. ^{1}H NMR spectra confirmed that all the vinylene groups were in *trans*-conformation because no peak appeared at 6.56 ppm

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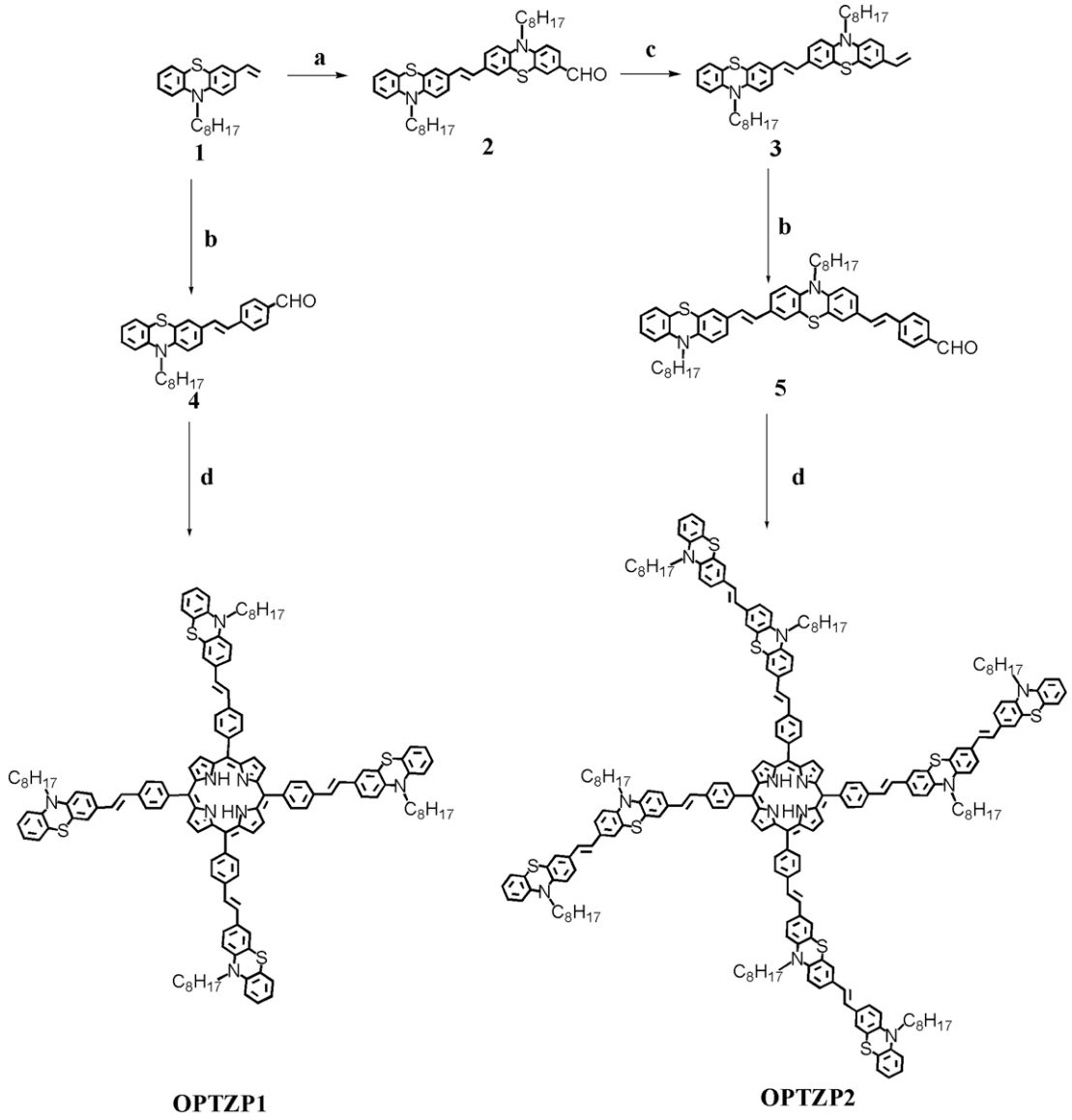

Scheme 1. Synthesis of the phenothiazine-functionalized porphyrins **OPTZP1** and **OPTZP2**. Reagents and conditions: (a) 3-formyl-7-bromo-10-octylphenothiazine, $Pd(OAc)_2$, K_2CO_3, DMF, Bu_4NBr, 110 °C, 12 h; (b) *p*-iodobenzaldehyde, $Pd(OAc)_2$, K_2CO_3, DMF, Bu_4NBr, 110 °C, 15 h; (c) Ph_3PCH_3I, *t*-BuOK, THF, rt, 12 h; (d) pyrrole, propionic acid, acetic acid and nitrobenzene, 135 °C, 2 h.

assigned to the proton in *cis*-double bond,[5] and the expected signals for the inner protons of the porphyrin moiety were located at −2.70 ppm. The MALDI/TOF-MS spectra also confirmed that the target porphyrins were generated, and some fragmentation peaks were due to the cleavage of *N*-octyl bonds.[5d,9]

Figure 1 shows the absorption spectra of **OPTZP1** and **OPTZP2**, several absorption bands in the visible region could be found, including four Q-bands in the 500–700 nm region (consistent with a free-base porphyrin) and Soret bands, other absorption bands between 300 nm and 400 nm were due to the peripheral phenothiazine–vinylene arms. We found that the Soret bands of **OPTZP1** and **OPTZP2** (ca. 435 nm, Table S1) were red-shifted compared to that of TPP (418 nm), this phenomenon can be attributed to the presence of an intramolecular donor-acceptor molecular framework as well as conjugation between the electron-withdrawing porphyrin unit and electron-rich oligophenothiazine–vinylene arms, which might decrease the energy gap.[10] As shown in Figure 2, the absorption spectra of **OPTZP1** and **OPTZP2** in the film were identical to those in the dilute solution except for slight red-shift,

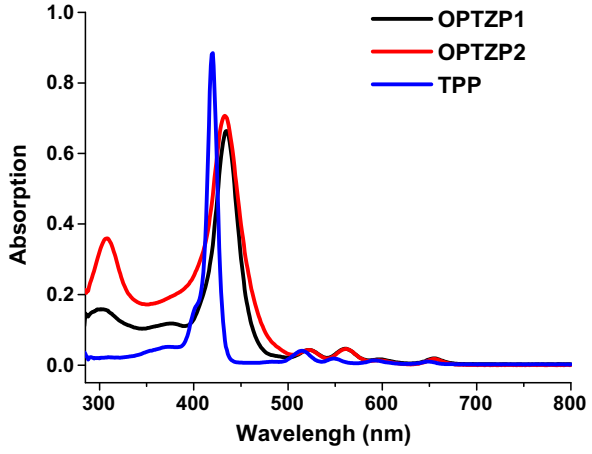

Figure 1. Absorption spectra of **OPTZP1**, **OPTZP2**, and TPP in toluene (2×10^{-6} mol/L).

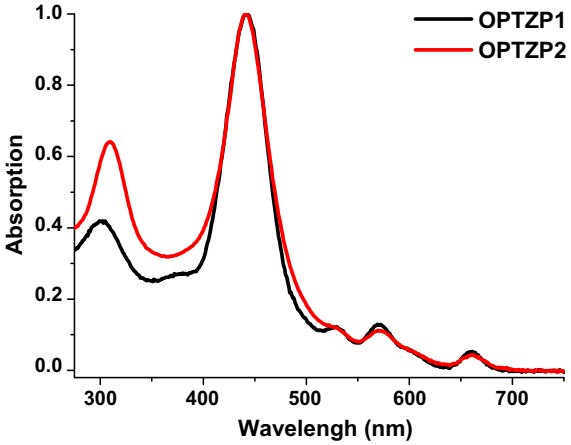

Figure 2. Normalized absorption spectra of **OPTZP1** and **OPTZP2** in the films.

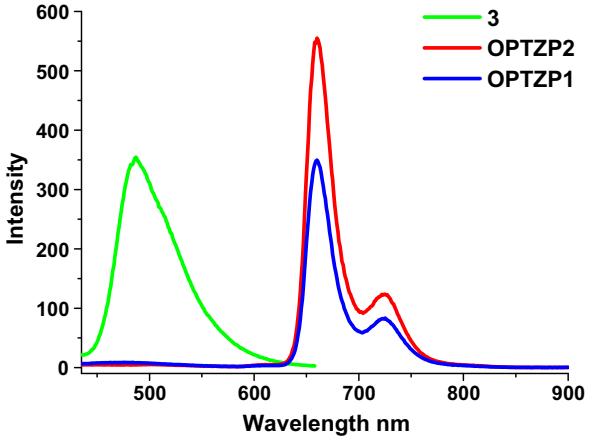

Figure 4. Emission spectra of compound **3**, **OPTZP1**, and **OPTZP2** in toluene (2×10^{-6} mol/L) excited at 295 nm.

which implied that intermolecular aggregation was suppressed in the films owing to the nonplanar conformation of phenothiazines.[4]

Figure 3 gives the fluorescence spectra of **OPTZP1** and **OPTZP2** in toluene excited at 435 nm, and the characteristic luminescence of the porphyrin cores at 662 nm appeared (Table S1). However, when the excitation wavelength of 295 nm, which could excite the phenothiazine–vinylene units instead of the porphyrin core, was selected, the emission at 662 nm due to the porphyrin cores could also be detected, while the feature emission from the phenothiazine–vinylene (the reference compound **3** could emit intense green light located at 500 nm under excitation at 295 nm as shown in Figure 4) was quenched. It suggested that the excitation energy of the phenothiazine–vinylene units might transfer to the porphyrin core. It was also found that the fluorescence intensity of **OPTZP2** was much higher than that of **OPTZP1**, illustrating that the light-harvesting ability of **OPTZP2** was improved compared with **OPTZP1** because of the multiplying of the number of phenothiazine units.[11] Figure S1 shows the fluorescence emission spectra of **OPTZP1** and **OPTZP2** in the films (excited at 440 nm), the porphyrins exhibited strong fluorescence emission and the emission bands were also slightly red-shifted from 662 nm to 666 nm (Table S1), indicating the phenothiazine ring was an excellent building block for impeding the aggregation and intermolecular excimer formation. The fluorescent quantum yields (Φ_F) were measured against TPP as the standard.[2c,11] The Φ_F values of **OPTZP1** and **OPTZP2** in toluene were 0.39 and 0.40, and in thin films were 0.35 and 0.37, respectively, which were much higher than most porphyrins reported, so they could be a good candidate for red-emitting materials.

In conclusion, we have synthesized two new porphyrins functionalized with monophenothiazine and diphenothiazine arms. The investigation of their photophysical properties revealed that the excitation energy of phenothiazine units could transfer to the porphyrin core and the obtained porphyrins could emit intense red light with higher fluorescence quantum yields than most porphyrins reported. They may possess potential applications in photonic devices.

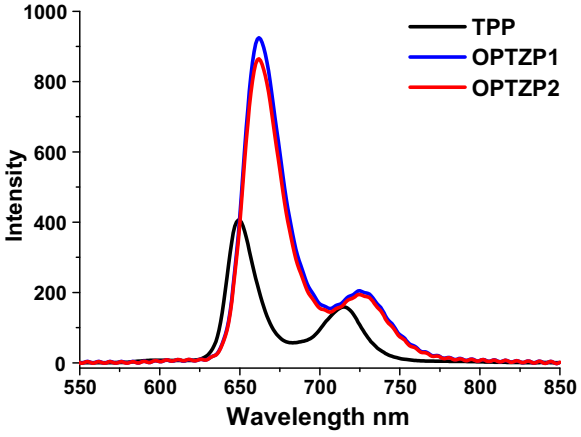

Figure 3. Emission spectra of **OPTZP1**, **OPTZP2**, and TPP in toluene (2×10^{-6} mol/L) excited at 435 nm.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.10.081.

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8. Compound **4**: ^{1}H NMR ($CDCl_3$, 500 MHz, ppm), δ 9.98 (1H, s), 7.85 (2H, d), 7.61 (2H, d), 7.30 (2H, t), 7.17-7.12 (3H, m), 6.98 (1H, d), 6.92 (1H, t), 6.88–6.6.83 (2H, m), 3.85 (2H, t), 1.84–1.78 (2H, m), 1.46–1.40 (2H, m), 1.33–1.25 (8H, m), 0.87 (3H, t). IR (KBr, cm^{-1}): 3020, 2919, 2851, 1693, 1593, 1463, 1370, 1250, 1166, 1043, 961, 857, 742. MALDI-TOF: calcd: 441.6, found: 442.3. Elemental Anal. calcd for $C_{29}H_{31}NOS$: C, 78.87; H, 7.08; N, 3.17; O, 3.62; S, 7.26. Found: C, 78.92; H, 7.11; N, 3.14.
   Compound **5**: ^{1}H NMR ($CDCl_3$, 500 MHz, ppm), δ 9.97 (1H, s), 7.84 (2H, d), 7.60 (2H, d), 7.31–7.21 (6H, m), 7.15–7.11 (3H, m), 6.98 (1H, d), 6.90 (1H, t), 6.86–6.79 (6H, m), 3.83 (4H, s), 1.83–1.78 (4H, m), 1.46–1.39 (4H, m), 1.31–1.25 (16H, m), 0.88–0.85 (6H, m). IR (KBr, cm^{-1}): 3019, 2922, 2851, 1694, 1595, 1467, 1362, 1248, 1164, 1037, 957, 855, 746. mp: 50.0–52.0 °C. MALDI-TOF: calcd: 777.1, found: 778.0. Elemental Anal. calcd for $C_{51}H_{56}N_2OS_2$: C, 78.82; H, 7.26; N, 3.60; O, 2.06; S,8.25. Found: C, 78.88; H, 7.24; N, 3.63.
   OPTZP1: ^{1}H NMR ($CDCl_3$, 500 MHz, ppm), δ 8.92 (6H, s), 8.20 (7H, d), 7.87 (7H, d), 7.46 (4H, s), 7.42 (4H, d), 7.30 (7H, s), 7.27 (5H, s), 7.19–7.17 (8H, m), 6.95 (4H, t), 6.91–6.89 (8H, m), 3.40 (8H, t), 1.89–1.83 (8H, m), 1.51–1.45 (8H, m), 1.38–1.29 (32H, m), 0.90 (12H, t), −2.70 (2H, s). IR (KBr, cm^{-1}): 3313, 3020, 2921, 2851, 1595, 1574, 1464, 1400, 1334, 1248, 1106, 964, 881, 800, 743. mp: 231.0–232.0 °C. MALDI-TOF: calcd: 1596.8, found: 1596.5. Elemental Anal. calcd for $C_{132}H_{130}N_8S_4$: C, 81.02; H, 6.70; N, 5.73; S, 6.55. Found: C, 81.06; H, 6.65; N, 5.77.
   OPTZP2: ^{1}H NMR ($CDCl_3$, 500 MHz, ppm), δ 8.90 (6H, s), 8.16 (7H, s), 7.83 (7H, s), 7.44 (4H, s); 7.39 (4H, d), 7.29–7.22 (28H, m), 7.14 (8H, m), 6.92–6.79 (28H, m), 3.86–3.82 (16H, m), 1.86–1.78 (16H, m), 1.48–1.40 (16H, m),1.33–1.26 (64H, m), 0.91–0.86 (24H, m), -2.69 (2H, s). IR (KBr, cm^{-1}): 3313, 3018, 2921, 2850, 1580, 1597, 1466, 1400, 1334, 1247, 1105, 958, 875, 800, 744. mp: 151.0–152.0 °C. MALDI-TOF: calcd: 3298.8, found: 3298.8; Elemental Anal. Calcd for $C_{220}H_{230}N_{12}S_8$: C, 80.10; H, 7.03; N, 5.10; S, 7.78. Found: C, 80.15; H, 7.06; N, 5.05.
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